Near Infrared Absorption of Ethylene between 8200 cm^{-1} and 9500 cm^{-1} to High Pressures and Temperatures

F. W. Nees and M. Buback

Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe

The near infrared absorption of pure ethylene in the region of the second overtone of the C-H stretching fundamentals (8200 cm^{-1} to 9500 cm^{-1}) was measured at supercritical temperatures ($T_c = 9.5$ °C) between 22 °C and 200 °C from 0.7 bar to 3000 bar.

The density and temperature dependence of bandshape, maximum frequency and absorption intensity are reported and discussed. The bands observed within a wide range of experimental conditions are assigned to combination and overtone modes.

The molar integrated intensity $\bar{B}_\lambda$ determined between the wavelength of maximum absorption and the high frequency absorption boundary was observed to be independent of pressure and temperature. This enables spectroscopic concentration determinations on ethylene in high pressure — high temperature phase equilibria and reactions.

Introduction

Spectroscopic experiments at high pressures and temperatures provide information about intermolecular interactions and enable qualitative and quantitative analysis to be made on systems under pressure. The quantitative aspect has been investigated in connection with high pressure ethylene-polyethylene mixtures in recent years [1−3]. The infrared absorption in the fundamental and first overtone region of the C-H stretching modes in ethylene has been measured between 22 °C and 200 °C to a maximum pressure of 3000 bar. The spectra taken in a wide density range permit the assignment of "overtone" bands positioned in the near infrared (NIR) between 5500 cm^{-1} and 6500 cm^{-1} to combination and overtone modes. The integrated molar absorption intensity of the $\nu_5 + \nu_9$ combination mode at 6138 cm^{-1} comes out to be independent of pressure and temperature. The band is thus well suited for ethylene determinations in high pressure-high temperature equilibria and reactions.

An extension of the spectroscopic technique on to the second overtone of the C-H stretching modes in C_2H_4 at about 8800 cm^{-1} seemed to be promising for two reasons:

(1) The C-H bands in ethylene and polyethylene are more separated in the higher overtones. Thus concentrations of both species may be determined with good precision simultaneously.

(2) Optical layer thicknesses of about 10 mm size may be employed for spectroscopic studies in the second overtone region, compared to 0.05 mm in the fundamental and about 1 mm in the first overtone region.

Layers of 10 mm size are easily calibrated and, moreover, allow a significant fraction of the pressurized substance to be transmitted by the NIR radiation.

The purpose of the present investigation is to determine the near infrared absorption of pure ethylene in the region of the second overtone of the C-H stretching modes between 8200 cm^{-1} and 9500 cm^{-1} at supercritical temperatures ($T_c = 9.5$ °C) from 22 °C to maximum temperatures of 200 °C. In order to obtain liquid-like densities, pressures up to 3 kbar were employed. The density and temperature dependence of bandshape, maximum frequencies and absorption intensities provide a basis for the assignment of observed bands to overtones and combination modes. The measured absorption intensities are analyzed with emphasis on quantitative work at high pressures and temperatures via near infrared spectroscopy.

Experimental

An optical high pressure cell [1] with two windows of colourless synthetic sapphire was used for the experiments. The spectra were recorded on a Cary 17H double beam spectrophotometer listing absorbances $A = \log_{10} I_0/I$ versus wavelength λ (in nm). I_0 and I are the intensities of reference and sample beams. Molar extinction coefficients ε (in cm^2/mol)

are calculated according to:

$$\varepsilon = \frac{M}{\varrho \, d} \, A$$

$M = 28.054$ g is the mole mass of C_2H_4, ϱ (in g/cm³) the experimental density [4] and d (in cm) the optical layer thickness. Pressures were measured with calibrated Heise-Bourdon gauges. The temperatures are read from Cr/Al thermocouples introduced into the high pressure fluid.

The maximum uncertainty in ε is below $\pm 2\%$ for densities above 0.35 g/cm³. It may be as large as 6% only for a few spectra taken at low density or at conditions close to the critical. The reported wavenumbers have an accuracy of ± 5 cm⁻¹ due to the occurence of rather broad bands.

Ethylene used in the experiments was of 99.85% purity. The ethane concentration amounts to about 0.11%. The oxygen concentration of 1.0 ± 0.1 ppm enables spectroscopic work on ethylene to 2 kbar even at 200 °C without any interference by a polymerization reaction [5].

Details of the optical cell, and its performance as well as a detailed error estimate are described elsewhere [3].

Results

The influence of pressure on the NIR absorption of C_2H_4 between 8200 cm⁻¹ and 9500 cm⁻¹ is illustrated by experimental absorbance spectra for 22 °C in Figure 1. The ethylene density varies from 0.00081 g/cm³ (0.7 bar) to 0.629 g/cm³ (3000 bar). The spectra are recorded at layer thicknesses of about 1 cm with exception of the 0.7 bar spectrum, which was measured in a quartz cell of 25 cm optical path length. The spectra show two domains of strong absorption centered around 8749 cm⁻¹ (1143 nm) and 8977 cm⁻¹ (1114 nm)*. Two bands of lower intensity occur at about 9120 cm⁻¹ (1097 nm) and 8615 cm⁻¹ (1161 nm). At the lowest pressures in Fig. 1 rotational subbands are observed for the individual absorption components. The P-, Q- and R-features collapse with increasing pressure. The 200 bar spectrum (0.4 g/cm³) shows two nearly symmetric bands at 8749 cm⁻¹ and 8977 cm⁻¹. The weak shoulders at 9120 cm⁻¹ and 8615 cm⁻¹ become more pronounced at still higher pressures such as 1000 bar (0.530 g/cm³) and 3000 bar (0.629 g/cm³). The 8749 cm⁻¹ band splits into two components at these high densities.

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* The position of absorption bands is characterized by the frequency of maximum absorption at an intermediate density of 0.4 g/cm³.
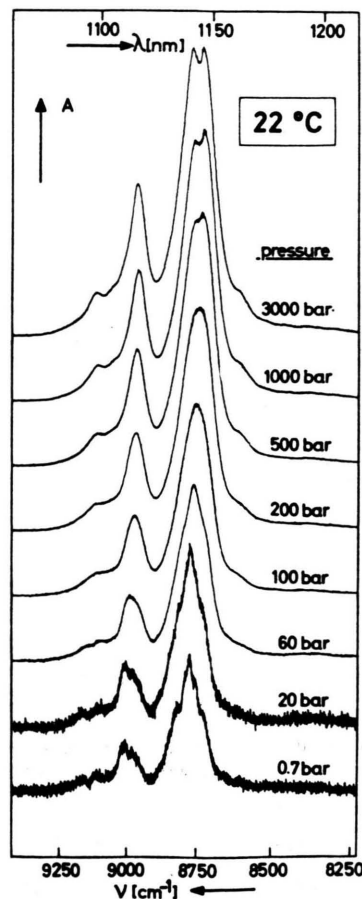

Fig. 1. Experimental NIR spectra of pure C_2H_4 from 8250 cm⁻¹ to 9500 cm⁻¹ for various pressures between 0.7 bar and 3000 bar at 22 °C. The layer thickness is 25 cm for the 0.7 bar spectrum and about 1 cm for the other ones. The spectra do not refer to the same absorption scale.

Experimental absorbance spectra in Fig. 2 demonstrate that at 200 °C a density of 0.50 g/cm³ corresponding to 2000 bar is not sufficient to cause a splitting of the main absorption band. The shoulders at 9120 cm⁻¹ and 8615 cm⁻¹ are less pronounced at 200 °C.

The molar extinction coefficient ε is shown as a function of wavenumber ν (in cm⁻¹) for several densities between 0.10 g/cm³ and 0.55 g/cm³ at 150 °C in Figure 3. The spectral features correspond to those observed previously (Figure 1, 2). At low density (0.1 g/cm³) envelopes of P-, Q- and R-branches occur. The splitting of the 8749 cm⁻¹ band is weakly indicated at 0.55 g/cm³ density. The absorption intensity of the bands between 0.10 g/cm³ (105 bar) and 0.55 g/cm³ (2500 bar) seems to be

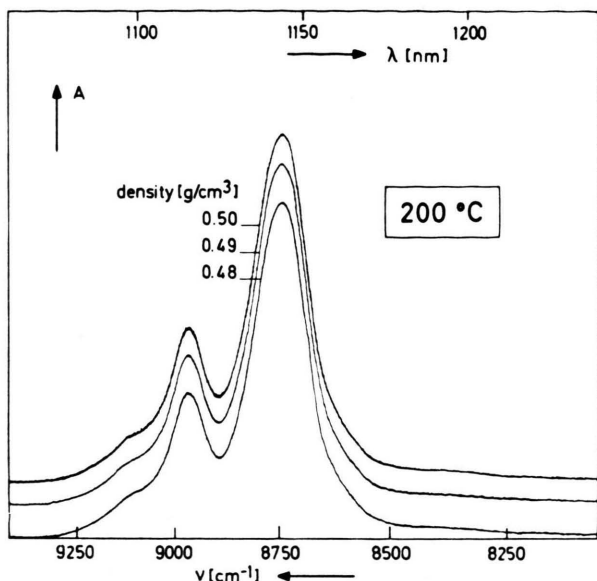roughly constant. The wavenumber of the absorption maximum shifts to higher values with decreasing density.

The frequency shift of the 8749 cm^{-1} (1143 nm) band maximum $\Delta\nu_{max} = \nu_{max} - \nu^0_{max}$ is plotted as a function of density in Figure 4. The reference wavenumber ν^0_{max} is taken at 0.05 g/cm^3 density. At

Fig. 2. Experimental NIR spectra of C$_2$H$_4$ for various densities between 0.48 g/cm^3 and 0.50 g/cm^3 at 200 °C.
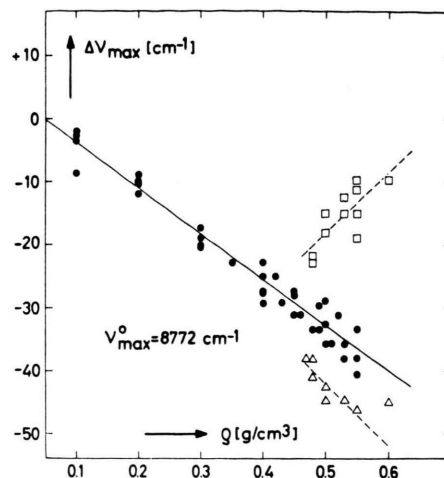

Fig. 4. Density dependence of the shift in band maximum $\Delta\nu_{max} = \nu_{max} - \nu^0_{max}$ for the 1143 nm (8749 cm^{-1}) component. The reference wavenumber ν^0_{max} is taken at 0.05 g/cm^3 density. The maximum wavenumbers are measured between 25 °C and 200 °C (circles). The squares and triangles are data at 25 and 60 °C for high densities.

densities below 0.47 g/cm^3 a straight line relation occurs which is independent of temperature within the limits of experimental error. The splitting is clearly observed at higher densities and temperatures below 110 °C.

Fig. 3. Molar extinction coefficient ε [cm^2/mol] of C$_2$H$_4$ as a function of wavenumber ν [cm^{-1}] for various densities between 0.10 g/cm^3 and 0.55 g/cm^3 at 150 °C
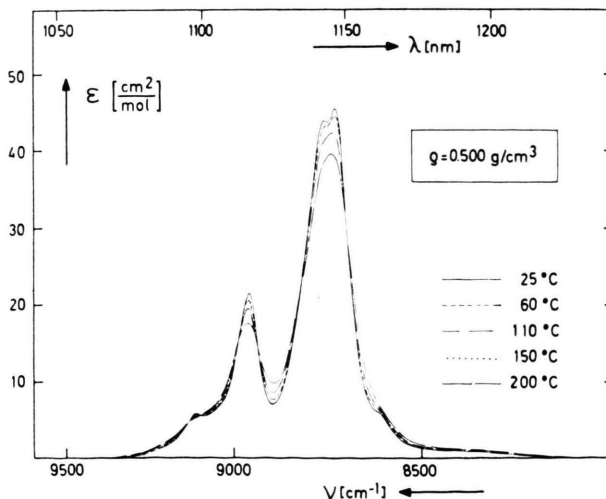
Fig. 5. Molar extinction coefficient ε [cm^2/mol] of C$_2$H$_4$ as a function of wavenumber ν [cm^{-1}] at constant density (0.50 g/cm^3) and various temperatures between 25 °C and 200 °C.

Molar extinction coefficients ε versus wavelength λ are given for a constant density $\varrho = 0.500\ \text{g/cm}^3$ at various temperatures between 25 °C and 200 °C in Figure 5. Increasing temperature reduces the splitting in the 8749 cm^{-1} band maximum. The molar extinction coefficients of the band maxima are diminished simultaneously, while the band half-widths increase.

Discussion

An important problem in NIR spectroscopy is the assignment of observed bands to combination and overtone modes. In the region of higher overtones several combinations may be positioned within a small frequency interval. The application of group theoretical arguments in combination with the study of the rotational P-, Q- and R-contours and of the variations in absorption intensities over a wide pressure and temperature range help to solve the band assignment problem.

Assignment of Ethylene Bands between 8250 cm^{-1} and 9250 cm^{-1}

The C_2H_4 molecule belongs to D_{2h} point group. None of the 12 non degenerate normal modes has an infrared active first overtone[6]. Among the second overtones five vibrations of B_{1u}-, B_{2u}- and B_{3u}-type symmetry are allowed in the infrared. Only two of them, $3\nu_9$ (B_{2u}) and $3\nu_{11}$ (B_{3u}), may contribute to the absorption between 8250 cm^{-1} and 9250 cm^{-1}. Obviously, more than two components occur in this frequency region (Fig. 1) and higher order combinations must therefore be considered for the band assignment.

At low density B_{2u}-components have P- and R-branches while B_{1u} and B_{3u} components, in addition, exhibit a Q-branch. Inspection of the 0.7 bar spectrum in Fig. 1 clearly indicates that the weak band at about 9130 cm^{-1} belongs to B_{2u}-type symmetry. The band is assigned to the $2\nu_1 + \nu_9$ (B_{2u}) combination mode. The absorption around 8987 cm^{-1} is identified as $2\nu_1 + \nu_{11}$ (B_{3u}) with contributions from the $3\nu_9$ (B_{2u}) second overtone absorption. The observed shift of the band maximum towards 8960 cm^{-1} at the highest pressure is consistent with the expected values for $2\nu_1 + \nu_{11}$ and $3\nu_9$.

The fine structure of the intense absorption at about 8772 cm^{-1} (0.7 bar spectrum in Fig. 1) indicates an overlap of Q-branched components. The decrease in band half-width due to the diminished

rotational freedom presumably gives rise to the band splitting at high pressure (Figure 1). The absorption is explained by an overlap of B_{3u}-species ($2\nu_{11} + \nu_3 + \nu_{12}$ and $3\nu_{11}$) with B_{1u}-species ($2\nu_5 + \nu_2 + \nu_7$ and $2\nu_9 + \nu_2 + \nu_7$). The contribution of ν_7 to the ternary combinations is highly probable as combinations involving ν_7 are known to be intense[6].

Contributions to the absorption between 8250 cm^{-1} and 9250 cm^{-1} by additional components cannot be excluded. The proposed assignment, however, seems to be adequate to explain the NIR absorption in this wavenumber region. For a more detailed band assignment, anharmonicity effects, Coriolis- and Fermi-type resonance must be taken into account.

Density and Temperature Dependence of Absorption Intensity

Concentrations of species participating in high pressure systems are favourably determined by spectroscopic means, if the characteristic absorption intensities are strictly proportional to density without any occurrence of specific pressure and temperature effects. The ethylene spectra were analyzed in order to find absorption characteristics of this type.

Usually concentrations are determined from the absorbance in the band maximum. The reduced absorbance A^r (1143 nm) $= (1/d) \cdot A$ (1143 nm) is plotted as a function of ethylene density for several temperatures from 25 °C to 200 °C in Figure 6. A (1143 nm) is the absorbance in the 1143 nm *
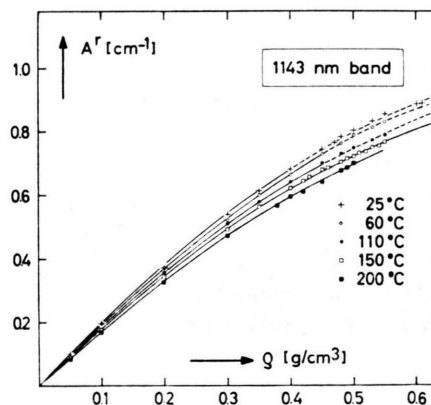

Fig. 6. Reduced absorbance A^r (1143 nm) in the 1143 nm band maximum as a function of density at various temperatures between 25 °C and 200 °C.

* The absorption bands are characterized by the wavelength value of the band maximum, as the experimental spectra which directly yield the intensities are plotted on a linear wavelength scale.

band maximum and d is the optical layer thickness. A^r (1143 nm) is not strictly proportional to the density and clearly depends on temperature (Figure 6). The decrease of A^r (1143 nm) with temperature at constant density will be due to rotational broadening. The curvature of the isotherms in Fig. 6 indicates a decrease of molar absorbance ($\sim A^r/\varrho$) with density. This effect results in part from the overlap of at least two bands, which are split at the highest densities (Figure 1). A^r (1143 nm) is hardly applicable for concentration determinations.

The density dependence of the reduced absorbance A^r (1114 nm) $= 1/d \cdot A$ (1114 nm) at the 1114 nm band maximum is shown for several temperatures from 25 °C to 200 °C in Figure 7. Density and
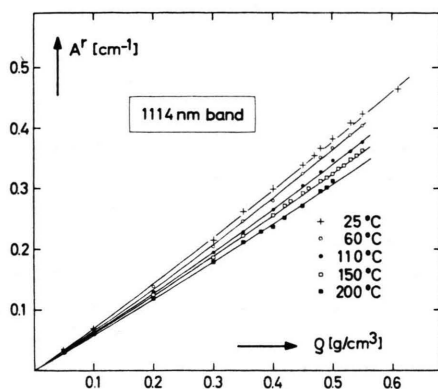
Fig. 7. Reduced absorbance A^r (1114 nm) in the 1114 nm band maximum as a function of density at various temperatures between 25 °C and 200 °C.

temperature effects on A^r (1114 nm) are clearly observed. The influence of increasing temperature and decreasing density on A^r (1114 nm) and on the molar absorbance ($\sim A^r/\varrho$) are in the same direction, contrary to the situation observed for the 1143 nm band. The behaviour of A^r (1114 nm) may be solely due to rotational broadening which is favoured by decreasing density and by increasing temperature.

The pronounced influence of rotational motion on the absorption intensity may disappear, when integrated absorption intensities are determined instead of absorptions in the band maxima. Inspection of Fig. 5 indicates that a decrease in maximum intensity and an increase in band half-width occur simultaneously. The integrated molar absorption in-

tensity might thus be independent of pressure and temperature.

The reduced integrated absorption intensity B_λ^r is plotted versus the ethylene density at five temperatures from 25 °C to 200 °C in Figure 8.

$$B_\lambda^r = \frac{1}{d} \int_{\lambda_1}^{\lambda_2} A(\lambda)\, d\lambda$$

λ_1 and λ_2 are the wavelengths of the absorption boundaries. Typical values are: $\lambda_1 = 1065$ nm (9390 cm^{-1}) and $\lambda_2 = 1220$ nm (8197 cm^{-1}). B_λ^r
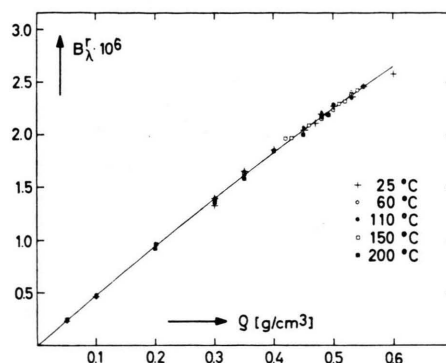
Fig. 8. Integrated intensity B_λ^r of the NIR absorption of C_2H_4 from 1065 nm to 1220 nm as a function of density at various temperatures between 25 °C and 200 °C.

is independent of temperature at constant density. The use of B_λ^r as an ethylene concentration measure is, however, somewhat restricted as the B_λ^r versus ϱ relation exhibits a slight curvature. The large wavelength region from λ_1 to λ_2 constitutes another serious limitation for concentration measurements via B_λ^r. Especially in mixtures with hydrocarbons

an appreciable absorption due to $-\overset{\mid}{\underset{\mid}{C}}-H$ frequencies makes a determination of B_λ^r exclusively due to ethylene absorption nearly impossible. For these reasons an absorption intensity $\overline{B}_\lambda^r$ is determined from a restricted region between the wavelength λ_m of the maximum of the band at about 1143 nm and the low wavelength boundary λ_1.

$$\overline{B}_\lambda^r = \frac{1}{d} \int_{\lambda_1}^{\lambda_m} A(\lambda)\, d\lambda .$$

The contribution of alcane absorption in this region is very small and may be easily corrected.

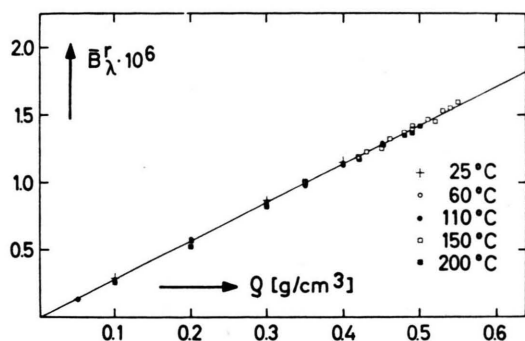$\overline{B}_\lambda^r$ is plotted versus the ethylene density for 25 °C, 60 °C, 110 °C, 150 °C and 200 °C in Fig-

Fig. 9. Integrated intensity $\bar{B}_\lambda{}^r$ as a function of C_2H_4 density at various temperatures between 25 °C and 200 °C.

the molar integrated absorption intensity $\bar{B}_\lambda$, which corresponds to the slope of the $\bar{B}_\lambda{}^r$ versus ϱ relation.

$$\bar{B}_\lambda = M\,\bar{B}_\lambda{}^r/\varrho \quad (M = \text{mole mass of ethylene}) \,.$$

A least squares fit of the $\bar{B}_\lambda{}^r$ values in Fig. 10 yields $\bar{B}_\lambda = (80.01 \pm 1.60) \cdot 10^{-6}\ \mathrm{cm^3\,mol^{-1}}$. The experimental quantity $\bar{B}_\lambda{}^r$ determined in pressure cells of about 10 mm layer thickness thus constitutes the desired absorption signal enabling concentration measurements on ethylene to be made to high pressures and temperatures. This result demonstrates the possibility of using NIR spectroscopy as a quantitative method of analysis with applications in technical processes.

ure 9. At 25 °C and 60 °C the intensity values for densities above 0.47 g/cm³ are omitted in Figure 9. Under these conditions the band splitting would introduce some subjectivity into the choice of λ_m. The data from numerous independent experimental runs fitted excellently onto a straight line passing through the origin. Within the experimental accuracy no temperature and density effects occur on

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